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Electrochemically Desulfurized Molybdenum Disulfide (MoS₂) and Reduced Graphene Oxide Aerogel Composites as Efficient Electrocatalysts for Hydrogen Evolution

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Recent developments in graphene related materials including molybdenum disulfide (MoS₂) is gaining popularity as efficient and cost-effective nanoscale electrocatalyst essential for hydrogen production. These “clean” energy technologies require delicate control over geometric, morphological, chemical and electronic structure affecting physical and electrochemical catalytic properties. In this work, we prepared three-dimensional hierarchical mesoporous aerogels consisting of two-dimensional functionalized graphene and MoS₂ nanosheets of varying ratio of components under hydrothermal–solvothetmal conditions ($P < 20$ bar, $T < 200$ °C). We systematically characterized these hybrid aerogels in terms of surface morphology, microstructure, understand heterointerfaces interaction through electron microscopy, X-ray diffraction, optical absorption and emission and Raman spectroscopy, besides electrochemical properties prior to and post electrochemical desulfurization that induces finely controlled sulfur vacancies. They feature enhanced electrical conductivity by means of eliminating contact resistance and meso-/nanoporous structure facilitating faster ion diffusion (mass transport). We demonstrate that controlled defects density, edges plane sites (nanowalls), mesoscale porosity and topological interconnectedness (monolithic aerogel sheets) invoked can accelerate electrocatalytic hydrogen production. For instance, low over potential with Tafel slope ~ 77 mV · dec⁻¹ for 60 wt.% MoS₂, highcurrent density, and good stability was achieved with desulfurization. These results are compared with continuous multilayer MoS₂ films highlighting the multiple role of tunable structure and electronic properties. The adjacent S-vacancy defects-induced increase in density of states, dissociation and confinement of water molecules at the pore edge and planar S-vacancy sites calculated using density functional theory helped in establishing improved heterogeneous electrocatalytic rate. This is supported with combined measurements of diffusion coefficient and heterogeneous electron transfer rate via surface-sensitive scanning electrochemical microscopy (SECM) technique.

Keywords: Graphene/MoS₂, Electrochemical Desulfurization, Sulfur Vacancy, Tafel Plots.

1. INTRODUCTION

Hydrogen (H₂) has been considered as a clean “green” and sustainable energy resource that can be easily generated via electrolysis and used without producing any greenhouse gases. Since the emergence of photocatalytic water splitting in 1972 [1], hydrogen evolution reaction (HER; $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$ in acidic medium and

$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$ in alkaline medium) by electrochemical catalysis have attracted enormous attention because it requires harvesting only water and useful for fuel cells as the reverse reaction [2–5]. According to the classic theory, HER proceeds through three principle kinetic reaction step involved within reductive half reaction of water splitting in acidic medium [6]:

$\text{H}_3\text{O}^+ + e^- \rightarrow \text{H}_{\text{ads}} + \text{H}_2\text{O}$ (Volmer reaction, discharge step)
(or $\text{H}^+ + e^- + \text{M (active site)} \leftrightarrow \text{MH}_{\text{ads}}$)

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$H_{ads} + H_3O^+ + e^- \rightarrow H_2 + H_2O$ (Heyrovsky reaction, electrochemical desorption step) or $(H^+ + e^- = MH_{ads} \leftrightarrow M + H_2)$

$H_{ads} + H_{ads} \rightarrow H_2$ (Volmer–Tafel reaction, recombination step) or $(2MH_{ads} \leftrightarrow 2M + H_2)$.

Thus, HER may occur via the Volmer–Heyrowsky mechanism or the Volmer–Tafel mechanism. In both cases, the reaction proceeds through hydrogen atoms adsorbed at the metal electrode surface sites, H_{ad} , and thus the rate of the overall reaction is influenced by the free energy of hydrogen adsorption as described by Parsons [7]. In electro- and heterocatalysis, the reactivity is correlated to adsorption energy. According to Sabatier principle, the interactions between catalysts and reactants should neither be too strong nor too weak, for reaction to proceed efficiently. If the hydrogen to surface bond is too weak, the adsorption step will limit the overall reaction rate and if otherwise (too strong), the desorption step will limit the overall reaction rate. To maximize the rate of the HER, a catalyst with appropriate surface properties must be employed. Currently HER involves utilization of expensive noble precious metals such as Pt, Pd and Rh or alloys in acidic medium [8, 9] as well as semiconductors including TiO₂ [10, 11], but high cost, global low availability and catalytic poisoning hinders their large-scale implementation [12–15]. Therefore, substantial technological advancements are necessary to make widespread implementation of water splitting that is economically viable. One critical requirement for HER is the development of highly electro active, stable electrocatalysts composed of earth-abundant materials, which are cost effective and can be produced using facile synthesis approaches [16]. Since then a plethora of activities involved in the development of cost-effective, noble metal free electrocatalysts [17] such as tungsten- [18], molybdenum- [19], cobalt- [20], iron- [21], and nickel-based materials [22–24]. However, most of these materials have had a large reaction overpotential (η) of 100–200 mV [25, 26]. Thus, design and development of efficient electrocatalysts for hydrogen productions, underpins several emerging clean-energy technologies.

Amidst two-dimensional layered transition metal dichalcogenide (TMD) such as naturally occurring molybdenum disulfide (MoS₂) and tungsten disulfide (WS₂), density functional theoretical (DFT) calculations by Hinnemann et al. [27] has demonstrated that the free energy of hydrogen adsorption (ΔG_H) for MoS₂ is ≈ 0.08 eV, which is close to thermo-neutral making MoS₂ potentially promising HER inorganic catalyst. This prediction was further confirmed experimentally on MoS₂ nanoparticles systematically varying terrace and edge site densities, where a linear correlation between the exchange current density and MoS₂ edge length was established. MoS₂ is a layered compound similar to graphite; each layer consisting of an atomic plane of Mo sandwiched

between two atomic planes of S with a 6.5 Å van der Waals gap separating each sheet in a two structural polytypes namely, trigonal prismatic (2H) and octahedral (1T) arrangement [28, 29]. It is a semiconductor with direct (indirect) band gap of 1.96 eV (1.2 eV). As a result, it possesses a variety of distinct surface sites and electron and hole mobilities approximately 2,200 times faster along a basal plane than perpendicularly between sheet [30]. Due to precious metal-free composition, MoS₂ represent a promising class of materials for making electrochemical hydrogen production feasible. The favorable properties for HER emanate from the presence of catalytically active sulfur atoms on the molybdenum edges planes with S vacancies (whereas basal plane, normally with completely coordinated sulfur atoms, is basically inert), high stability in strong acids and an advantageous band gap aligned with the hydrogen redox potential [31–35]. The observation of MoS₂ edge activity for the HER has opened new avenues for increasing catalyst performance and efforts are particularly focused on exposing catalytic edge sites by engineering the morphology (amorphous, flower-like nanosheets, micro-boxes and nanoparticles, molecular cluster forms) of MoS₂ and by optimizing the basal plane to edge plane sites ratio. Several routes for improving the density of accessible edges at the surface of TMDs have been proposed, evaluated and compared [36–38]. The typical engineering the surface of the catalysts is to expose edges, or introducing structural defects to create new surfaces with edges by creating holes or nanovoids. Alternate ways are creating vertically aligned nanosheets, nanowalls since in-plane conductivity is 2–3 orders of magnitude is higher than out of plane configuration between the layers. Although a plethora of active edge sites is beneficial, the vertical charge transport through layers is an important limitation in HER performance, which must be addressed while developing MoS₂ based electrocatalysts with optimum performance. The combined increase in unsaturated sulfur edge sites and enhanced electron transfer accrued from the optimized layers for enhances catalytic activity. Moreover, there are three different techniques suggested to optimize the HER activity of MoS₂ include: (1) via defects engineering in MoS₂ nanosheets to increase the catalytic activity of the activity sites, (2) in improving the electrical contact to these sites by strategic selection of support material; the choice of substrates influences the energy of hydrogen adsorption to a thermo-neutral value; (3) increasing the number density of active sites of the catalysts by means of increasing effective surface area; and finally, (4) intrinsic conductivity of semiconducting 2H MoS₂ can be enhanced via edge sites without inducing structural phase transformation [39]. These postulations are substantiated by several reports from the existing literature mentioned above. Rational control of geometric, topologic, structural, electronic, and chemical properties is an important issue for their dedicated applications including electrochemical

energy (conversion, storage and harvesting) systems as well as electrosorption, sensing and electrocatalysis [40]. While there are several new reports, it is recognized that the development of electrocatalysts has been essentially empirical. Moreover, there remains a gulf between those who develop electrode materials and those who seek to understand the surface of electrocatalysts and heterogeneous electrocatalysis process.

In this work, we assembled “hybrid” ensemble of conductive graphene nanosheets supported MoS₂ nanostructures and interlaced graphene and MoS₂ nanosheets network via facile hydrothermal–solvothetical synthesis with varying component ratio for structural and phase optimization. The interaction between chemically reduced graphene oxide (CrGO) and MoS₂ is systematically studied with complementary techniques to show creation of emergent hetero-interfaces with desirable combined physical (higher electrical conductivity, mechanical strength) and chemical properties (higher specific surface area, faster diffusion or mass transportation, facile electron and ion transportation). The electrocatalytic and advanced electrochemical microscopy studies are conducted in view of fundamental insights into interfacial processes supplemented with hierarchical mesoporous and topological interconnectedness, invoked in synthesized reduced graphene oxide–MoS₂ monolithic aerogels (GA–MoS₂, hereon) with finely tuned surface structure and enhanced heterogeneous electron transfer rate (k_{ET}). We also amplified the typical data collected for the electrochemical HER such as overpotential by precise control of basal and edge site defects density via electrochemical desulfurization of MoS₂ nanosheets. The applied desulfurization potential and operating duration is varied for controlled HER activity. Defects in solids dramatically perturb the local density of states (LDOS) and create additional energy levels between the valence and conduction bands. Only a very limited number of investigations have focused on understanding and elucidating the role of defects that can potentially open new directions for increasing the conductivity and density of active sites of basal planes of the nanosheets. For this purpose, while a direct comparison of the catalytic performance of the basal and edge sites of nanosheets remains challenging due to the large difference in electrical properties between the metallic edges and the semiconducting basal plane, here in this study we attempted to fulfill these gaps using advanced electrochemistry. The GNS–MoS₂ composites displayed a unique 3D architecture leading to high catalytic performance with low overpotential, reasonably good stability, high current and active site density. This unique method of tuning the properties of MoS₂ is promising for creating noble metal-free catalysts. The results are also compared with continuous few-layer MoS₂ prepared from monolayer MoS₂ dispersions on gold coated silicon substrates and graphite rod. Additionally, density functional theoretical (DFT) calculations are performed for MoS₂/graphene hybrid system in

terms of density of states with and without adjacent and non-adjacent S-vacancies in hydrated environment highlighting the defect-induced increase in density of states (midgap states), confined water molecules and dissociation of water molecules at the adjacent S-vacancy sites on basal or edge planes. Finally, potential for future noble-metal free electrocatalyst designs based on topological and quantum materials are mentioned.

2. EXPERIMENTAL DETAILS

2.1. Materials and Methods

2.1.1. Preparation of GO

GO was prepared by modified Hummers’ method referring to our previous work and was dispersed in deionized (DI) water by ultrasonication to give a stable brown dispersion [20].

2.1.2. Preparation of Aerogels and Films

The graphene and graphene–MoS₂ aerogels were synthesized using hydrothermal–solvothetical method using two separate dispersions followed by mixing them for hybrids (see Fig. 1 schematic). The first dispersion was graphene oxide (GO), where 400 mg GO powder was dispersed in 200 mL DI water to create 2 mg/mL concentration. This solution was ultrasonicated for 4–6 hours to ensure well-dispersed homogeneous solution with no large or small GO flakes. 1.1 mL of ethylenediamine (EDA) was mixed into GO dispersion for cross linking and as surfactant. The second dispersion was made by creating 200 mL mixture of 45% isopropyl alcohol (IPA) and 55% DI water. Then 800 mg of molybdenum disulfide (MoS₂) was dispersed with DI (400 mL) to produce 4 mg/mL concentration dispersion and ultrasonicated for an hour before adding 2.2 mL of EDA. These two solutions were then mixed in varying volume to obtain a range of MoS₂ concentration i.e., 40%, 60%, 80%, and 90% wt.% and ultrasonicated for an hour for homogenization. Additionally, GO and MoS₂ dispersion with EDA were also used to prepare graphene and MoS₂ aerogels by themselves as control. The GO and MoS₂ dispersions were placed into a box furnace at 180 °C for 16–18 hours and the mixtures (GO/MoS₂) with varying concentration of MoS₂ were all heated at 180 °C for 24 hours. All the solutions were cooled normally, taken out of furnace and 0.33 μ L monohydrate hydrazine was added for every 40 mL solution. All of the dispersions were placed back in the furnace for 12 hours at 90 °C. Upon completion, all the dispersions are in hydrogel state. To remove the moisture and bulk water, the hydrogels were freeze dried at –30 °C for at least 72 hours to sublime the fluid out and transition them into aerogels. These aerogels were then thermally processed for 3 hours in vacuum oven at 160 °C to remove the remaining water molecules (see Fig. 1, panel A). To prepare electrodes, we crushed these aerogels and made a paste by adding *N*-methyl-2-pyrrolidone (NMP) organic solvent dropwise to create

Figure 1. (A) Hydrothermal synthesis scheme for graphene-MoS₂ 'hybrid' aerogels and continuous films. (B) SEM images of MoS₂, CrGO, 40, 60, 80 and 90 wt.% MoS₂ aerogels along with multilayer MoS₂ from monolayer MoS₂ and precursors GO and rGO_{th}. Some of the images are falsely colored to depict apparent morphology of aerogels.

slurry, which was spread over conducting (stainless steel and ITO coated glass) substrates as films and air dried overnight (see Fig. 1, panel A). In addition to aerogels, a solution of GO 2 mg/mL and monolayer MoS₂ 4 mg/mL concentration were drawn into a syringe and spread onto gold and stainless-steel substrates, allowed to dry, leaving GO and MoS₂ nanosheets/flakes. This process was repeated 4 times, so continuous thin films of raw precursors GO and monolayer MoS₂ nanosheets are formed for comparison (see Fig. 1, panel A).

2.1.3. Electrochemical Desulfurization

The MoS₂ samples were electrochemically desulfurized to remove sulfur in order to improve electrocatalytic activity in amperometry mode at several potentials -0.5 V, -0.6 V, -0.8 V, -1.0 V, -1.6 V, -1.9 V, and -2.0 V versus RHE each for 10 min monitoring current or current density prior to stability tests that was conducted at constant potential of -0.32 V versus RHE for 8 h.

2.2. Characterization

2.2.1. Microstructure and Electrochemical Properties

All the samples were characterized using complementary techniques to reveal surface morphology, microstructure and lattice vibration properties. Scanning electron microscopy (SEM) images were taken with an instrument (Model JSM-6510LV, JEOL Ltd., Peabody, MA, USA) operating at a primary electron acceleration voltage (V_{acc}) of 15 kV at constant current 45 μ A in secondary electron imaging (SEI) mode with a LaB₆ filament. For transmission electron microscopy (TEM), a few flakes were distributed onto commercial lacey carbon coated Cu grids (Ted Pella, Inc. CA). TEM images were taken using a JEOL instrument (Model 1400 Plus, OR) operating in cryo-EM and SAED modes at 100 kV and 1 nA from LaB₆ gun with a Be specimen holder, a Gresham SiLi detector with Moxtek AP3.3 window and with AMT 8 Mpixel cooled camera. For SAED patterns, we used 0.10 μ m aperture producing a small spot size and spread the beam to increase the electron coherence length at the samples. TEM measurements provided nanoscale morphology and intrinsic microstructure that help to determine interplanar spacing from selected area electron diffraction (SAED) patterns. X-ray diffractograms (XRD) were collected on a powder diffractometer (Bruker Model D8 ADVANCE, Bruker) using Cu K α radiation ($\lambda = 1.5406$ Å) in $2\theta = 10$ – 80° with a step 0.02° . The UV-Visible absorption and fluorescence spectra were measured using optical spectrometer (BioTek Model Synergy H1 Multi-mode Reader, Winooski, VT) equipped with a Xenon lamp as broadband excitation source. For fluorescence and photoluminescence excitation (PLE) spectra, the excitation wavelength λ_{ex} used was scanned from 300 nm–600 nm with 30 nm interval and spectra were measured with 0.5 nm step size in the range 350–650 nm and UV-Vis absorption spectra is

measured between 230 nm and 800 nm in interval of 1 nm. All of the measurements were carried out at room temperature.

Raman spectra were acquired to determine lattice bonding variation, chemical composition and structural phases of graphene and MoS₂ nanostructures. The spectra were measured using a micro-Raman spectrometer (Model In Via Renishaw plc, Hoffman Estates, IL, USA) equipped with a laser providing excitation wavelength 633 nm (or energy $E_L = 1.92$ eV). The reflected light is filtered using edge filter to remove laser excitation cutting at ~ 100 cm^{-1} and sent to the spectrometer. The scattered light from the sample is collected in backscattering geometry transmitted and detected by CCD camera. An objective lens of 50 $\times$ was used providing a spot size of ~ 1 – 2 μ m and the laser power on the sample is maintained between <0.1 – 0.5 mW (1 or 5%) using neutral density (ND) filters to avoid local heating effects preventing photothermal degradation. The Raman spectra were acquired from 120–180 s depending upon the laser power used and to maximize throughput signal. Raman spectra ranged from 120– 3200 cm^{-1} for MoS₂ samples and 1100 cm^{-1} to 3200 cm^{-1} for graphene-related aerogel samples with spectral resolution 1 cm^{-1} . The optical microscope stage of Raman spectrometer is piezo-controlled that allows mapping Raman spectra. The acquisition time per pixel was a few minutes to an hour in case of Raman mapping with step size 0.10 μ m (or 200 nm) for an area of 20×20 μm^2 to elucidate components homogeneity through intensity distribution of specific Raman peaks.

A custom designed single compartment three-electrode electrochemical cell was used for electrochemical measurements, using an electrochemical workstation (Model CHI920D, CH Instruments, Austin, TX, USA) in cyclic voltammetry (CV), linear sweep voltammetry (LSV) and impedance spectroscopy (EIS) modes. The three electrodes include Ag/AgCl reference electrode, a Pt wire counter electrode and the aerogel samples as working electrode. The CV and LSV were measured in 0.1 M H₂SO₄ base electrolyte in the potential range -1.5 V– $+0.5$ V at various scan rates $v = 5, 10, 20, 50$ and 100 mV/s. Impedance spectroscopy and chronopotentiometry (charging/discharging) tests were ran at 1 μ A, 10 μ A, 50 μ A, 100 μ A, 500 μ A and 1 mA. After post-desulfurization of MoS₂-based samples, all the electrochemical measurements were performed in a similar manner. Scanning electrochemical microscopy (SECM) was performed to probe electrode/electrolyte interface and to capture information about electrochemical (re)activity. The samples were coated on gold and stainless steel substrates and tested in base electrolyte 0.1 M H₂SO₄ and 0.5 M PBS with 5 mM K₃Fe(CN)₆ (potassium ferricyanide) redox mediator. Measurements in microelectrode configuration included cyclic voltammetry at scan rates $v = 10, 20$ mV/s, probe approach with tip voltage $V_t = +0.5$ V and substrate

voltage $V_s = -0.4$ V (polarity 1; pol1) and $V_s = +0.4$ V (polarity 2; pol2) to determine heterogeneous electron transfer rate (k_{ET}), and SECM imaging with these polarities in probe area $250\ \mu\text{m} \times 250\ \mu\text{m}$ with $2\ \mu\text{m}$ increment [41, 42]. Samples desulfurized at -0.5 V and 2.0 V were produced for SECM related measurements with the same parameters for comparative study.

2.3. Computational Methods

2.3.1. Periodic Slab Modeling

MoS₂ Modeling. Pristine 2H MoS₂ three-layer slab is modeled as two-dimensional 4×4 hexagonal lattice with 16 atoms per layer in the unit cell (48 atoms in total). Here, the S atoms occupy the top and bottom MoS₂ layers and Mo resides in the middle layer. Figure 10(A) shows the geometrically optimized unit cells for hydrated pristine and defective MoS₂ with S vacancies. The S vacancies are mimicked by removing S atoms from the MoS₂ lattice. Non-adjacent S vacancies are modelled using the 4×6 supercell, where in its pristine phase it contains 72 atoms (Fig. 10A(d)). Hydrated pristine MoS₂ configurations are built as follows: the H₂O + MoS₂ configuration is obtained by initially placing a single water molecule in the vicinity of the MoS₂, followed by geometry optimization. The $2 \times \text{H}_2\text{O} + \text{MoS}_2$ is obtained by using the optimized structure of the H₂O + MoS₂. In this case, a second water molecule is placed in the vicinity of the H₂O + MoS₂, followed by geometry optimization. The process is repeated for up to 6 water molecules.

MoS₂/Graphene Modeling. The MoS₂/graphene heterostructure unit cell consists of two hexagonal lattices as follows: The 2H MoS₂ three-layer 4×4 lattice with S atoms occupying the top and bottom MoS₂ layers and Mo atoms residing in the middle layer (48 atoms) overlaid on a $3\sqrt{3} \times 3\sqrt{3}R30^\circ$ monolayer graphene (54 atoms). Here, the MoS₂ bottom S layer is the one closer to graphene. Our MoS₂/graphene heterostructure is similarly to the one reported by Shao et al. [43]. Figure 1(B) shows the DFT optimized MoS₂/graphene unit cells with and without S and C vacancies for hydrated MoS₂. Here, the S vacancies are located on the MoS₂ top layer. Defective MoS₂/graphene structures are built by considering combinations of single and non-adjacent double S vacancies MoS₂ with a single C vacancy in graphene. We also consider defective MoS₂/graphene structures, with MoS₂ being pristine paired by a defective graphene and vice versa.

Density Functional Theory (DFT) Calculation Parameters. CRYSTAL17 [44] code is used to calculate the optimized geometries and electronic properties for dry and hydrated systems. An advantage of CRYSTAL is its treatment on two-dimensional slabs, without the need of artificial periodicity perpendicular to the surface, which is typically found in other DFT codes [45]. Periodic restricted DFT is used here as in our past work [46, 47]. We used PBE0

non-empirical/parameter-free functional [48, 49]. For comparison, selective calculations use the screened hybrid functional HSE06 of Heyd, Scuseria and Ernzerhof, which provide band gaps that better agree with experiments [50]. All calculations are treated using the D3 semiempirical correction by Grimme et al. [51]. This correction improves the DFT functionals description of the long-range electron correlations that are responsible for van der Waals interactions between the waters and MoS₂. All atoms are described by all-electron basis sets, which are optimized for crystalline calculations. The S and H atoms are treated by the pob-TZVP basis sets from Peintinger et al. [52] and the O atoms by the split-valence 8-411G (2d1f) basis set from Mahmoud et al. [53]. Effective core potentials (ECP) are used for Mo atoms and Mo valance is described by (3s2p2d1f) basis set [54]. For geometry optimizations, Brillouin zone integrations (Monkhorst-Pack grid) [55], the Fermi energy, and the density matrix calculations (Gilat grid) [56] are performed on a 12×12 and 6×6 grids, for MoS₂ and MoS₂/graphene heterostructures, respectively. The Fermi surface is smeared with a Gaussian of 0.005 Hartrees for convergence purposes. Moreover, the SCF (self-consistent field) energy convergence is achieved using Anderson quadratic mixing [57], coupled with additional mixing of the occupied with the virtual orbitals. The SCF energy threshold value for our calculations is set at 10^{-9} Hartrees (default value is 10^{-7} Hartrees). For hydrated MoS₂, charge transfers between the waters and the support are calculated using both the iterative Hirshfeld population [58], which is based on the atoms in molecules (AIM) approach [59, 60]. Hirshfeld populations are less basis-set depended than Mulliken [61] and smaller in magnitude (relative to Mulliken) [62]. The stabilities of the final geometries are secured via post-geometry optimizations.

3. RESULTS AND DISCUSSION

3.1. Morphology Control of Graphene-MoS₂ Aerogels

We prepared 3D mesoporous MoS₂@GNS hybrid nanosheets by mixing them in certain ratio of the components. The rich surface of GO with oxygenated functional groups are partially reduced thermally/chemically (CrGO) and they also induce strong interaction between the two types of nanosheets forming MoS₂-GNS hybrids. Finally, the hybrid nanosheets were treated with hydrothermal/solvothermal method to form 3D mesoporous architectures of MoS₂@GNS aerogels. The interaction between the 2D materials is critical to prohibit restacking during ensemble fabrication. In this work, the use of monolayer MoS₂ nanosheets expectantly increased the interaction between the component materials resulting in stable 3D architectures without obvious restacking of the composites with relatively high MoS₂ content. Figure 1(B) shows a series of field emission scanning electron microscopy (FESEM) images of chemically reduced graphene oxide

(CrGO), MoS₂, 40, 60, 80, 90 wt.% MoS₂ hybrid aerogels in addition to multilayered MoS₂, GO and thermally reduced rGO as precursors revealing surface morphology and microstructure prior to desulfurization. Some of the images are falsely colored to emphasize graphene nanosheets (blue) coated with or interlaced with MoS₂ nanostructures (dust yellow). As shown in Figure 1(B), the content of MoS₂ in aerogels play an important role in tuning the morphology and microstructure such that pure graphene aerogels reveal a 3D porous structure constructed by interconnected large lamellar nanosheets with micropores ranging from sub-micrometer to tens of micrometers. With increasing MoS₂ content, the composite aerogels exhibit a well-constructed 3D foam structure with uniform pores of several nanometers to micrometers and many smaller hybrid nanosheets as building blocks. It is worth noting that the 3D porous architecture of the composite aerogels was retained even when the MoS₂ content reached 90 wt.%, exhibiting greatly improved structural stability than that of the previously reported structures [36]. While we also measured some of the images post-desulfurization, no noticeable differences were observed within SEM resolution (not shown). The nanoscale morphology and microstructure of the 3D MoS₂@GNS hybrid aerogels are further investigated by TEM and the images are shown in Figure 2(A) besides selected-area electron diffraction (SAED) patterns and integrated intensity with interplanar spacing provided in Figure 2(B). The TEM images in Figure 2(A) further validates the 3D porous architecture of graphene only aerogels (CrGO) and with increasing MoS₂ content, hierarchical porosity with gauzy form prevails. The relatively higher resolution TEM images show clear MoS₂ nanosheets anchored on and/or within graphene nanosheets forming hybrid porous nanosheet heterostructures with many exposed edges. Diffraction rings in the SAED pattern result from (110) and (100) planes of graphene sheets and MoS₂ indicated with G and M, respectively. The absence of hkl with $l \neq 0$ in the SAED pattern is due to the fact that the c axis of both rGO and MoS₂ sheets attached to them are nearly parallel with the electron beam. The lattice fringes are clearly observable and the interplanar spacing is deduced to be 6.25 Å, corresponding to the (002) crystal plane of MoS₂. The distinct hexagonal lattice structure suggests that the materials are highly crystalline. A majority of the nanosheets were found to be 200–300 nm in lateral dimensions and exhibited typical thickness of 1–1.2 nm. It is noteworthy that the SAED pattern for MoS₂ and WS₂ showed d_{100} of 0.270–0.275 nm and d_{110} ~0.15–0.16 nm. In general, the findings from HRTEM in conjunction with SAED are in strong confidence that are cross-correlated with X-ray diffraction (XRD) to interpret the phase and structure. XRD peaks corresponding to MoS₂/rGO shown in Figure 3(a) are centered at $2\theta = 11.7^\circ, 14.3^\circ, 33.6^\circ, 40.1^\circ, 49.1^\circ, 59.0^\circ$, and 69.4° which are indexed to (002), (100), (103), (006),

(105), (110) and (008) atomic crystal planes of hexagonal graphene and MoS₂ (JCPDS No. 37-1492) phase, respectively. It is noticed that the peak position at 13.9° corresponds to (002) plane shifts to the left compared with that (14.4°) of the normal MoS₂ indicating that the distance between the (002) plane increases, which is in good agreement with the interplanar spacing measured in TEM images. Except for (002) peak, other peaks have marginal shifts since changes in interplanar spacings and lattice parameters ($a = 3.15$ and $c = 12.3$ Å) are too small (see Fig. 3(b)).

3.2. Structural Properties of Graphene-MoS₂ Aerogels

The optical properties were studied by ultraviolet-visible (UV-Vis) absorption and photoluminescence emission (PLE) spectroscopy. The absorption spectrum of a material generally yields a reliable measurement of the bandgap in situation where PL appears to be indirect, either in configuration space or in momentum space. The recorded UV-Vis absorption spectra for the aerogel dispersions is provided in Figure 4, panel A. An obvious broad peak located at ~270 nm is observed which is somewhat in contrast with the large lateral dimension of 2D MoS₂ that shows known peaks at ~609 nm and ~668 nm ascribed to B and A direct excitonic peaks, respectively, arising from the K point Brillouin zone [63]. However, zoomed in version of the absorption spectra shows very weak exciton peaks (quenching of PL with thickness, defects etc.) for the higher MoS₂ content aerogels. Alternatively, weak interlayer coupling between the restacked MoS₂ nanosheets due to possible rotational stacking disorder suggested by TEM images is responsible for the gradual decrease in PL. The strong blue shift in the optical absorption may be due to the quantum size effect [64] and the broad absorption at 268 nm is attributed to the blue-shifted convoluted Z, C, and D excitonic peaks [65]. The photoluminescence excitation (PLE) spectra for a series of MoS₂ aerogel samples including GO precursor and MoS₂ monolayer are recorded with varying excitation wavelength shown in Figure 4(B) along with PLE intensity maps. The strongest luminescence displays strong sharp peaks at 450 nm (2.76 eV) due to direct transition from deep valence to conduction band, which shifts with excitation wavelength, and weak sharp peak at 268 nm (4.63 eV). Similarly, the maximum emission peak centered at 530 nm with some variation depending upon the reduced graphene oxide content can be seen in PL spectra excited at 450 nm. This differs from the two well-known peaks centered at ~610 and ~661 nm in larger 2D MoS₂ flakes from direct band gap hot PL from the K point. The strongly blue-shifted hot PL from the K point is assigned to smaller lateral dimension of MoS₂ aerogel sheets owing to quantum size effect similar to MoS₂ [65] and graphene quantum dots [66].

Unlike semi-metallic graphene, the MoS₂ is a semiconductor with larger direct bandgap as shown above, the

Figure 2. (A) TEM with selected-area electron diffraction (SAED) images of MoS₂, CrGO, 40, 60, 80 and 90 wt.% MoS₂ aerogels revealing morphology and microstructure (Scale bars are shown at the bottom of the images) (B) Corresponding real space (d_{hkl}) intensity pattern revealing crystal structure of CrGO, MoS₂, 40, 60, and 90 wt.% MoS₂ aerogels. For SAED an aperture (0.23 μ m) in Köhler condition was used for small spot size and spread beam to increase the electron coherence length at the samples. Schematic example of the origin of the superstructure in real space and reciprocal space for MoS₂, graphene and heterostructure.

Figure 3. (a) X-ray diffraction (XRD) pattern for as-synthesized MoS₂-based aerogels and (b) corresponding fractional change in interplanar spacing for three different peaks with increasing MoS₂ content.

presence of which opened a realm in the area of electronic and photonic devices. Thermodynamically stable form of MoS₂ is the trigonal prismatic (2H-MoS₂) phase where each Mo atom is prismatically coordinated by six surrounding S atoms with symmetry space group of bulk MoS₂ as P3m1 (point group D_{6h}) [67, 68]. The space group of a single layer is P6m2 (point group D_{3h}). Consequently, systems with even numbers of layers belong to the space group P3m1 (with inversion symmetry), and systems with odd numbers of layers to the P6m2 space group (without inversion symmetry) [69]. The representative Raman spectra are shown in Figures 5(A)–(C) besides Raman mapping analysis. There are notably four first-order Raman active modes present in most reported MoS₂ Raman spectroscopic studies namely, E_{1g} (~286 cm⁻¹), E_{2g}¹ (~383 cm⁻¹), A_{1g} (~408 cm⁻¹), and E_{2g}² (~32 cm⁻¹). All the first-order bands are a result of vibration modes within the S–Mo–S layer, except for the E_{2g}² (~32 cm⁻¹) band which is due to the vibration of the adjoining rigid layers. Since the direct transition is located at 1.95 eV (635.9 eV), the matching of the excitation laser photon energy (633 nm or 1.92 eV) used causes strong coupling of energy into lattice phonon modes. This resonance can combine with the four first-order Raman frequencies creating additional energy states that can be excited, resulting in a variety of new second-order Raman lines (Fig. 5(A), left). With this most of the second-order bands observed are combination of longitudinal acoustic (LA) mode and first-order Raman bands. For example, the spectrum taken with 633 nm, there is a larger band at 466 cm⁻¹ which can be attributed to twice the LA(M) mode at 232 cm⁻¹. The 645 cm⁻¹ band is a combination of the LA(M) and the A_{1g} wavenumber (~410 cm⁻¹) at point M. The two prominent lattice vibrational modes having symmetries E_{2g}¹ arising due to in-plane vibration at ~382 cm⁻¹ and A_{1g} is from out-of-plane vibration of S atoms at ~400 cm⁻¹. Raman modes is sensitive to thickness dependence, with the wave

number of E_{2g}¹ decreasing (softens) and that of the A_{1g} (or A₁) increasing (stiffens) with thickness. Frequency difference (Fig. 5(B), right) of these two Raman modes are related to number of layers [70]. While MoS₂mono sample shows two or three-layers since the difference is larger than ideal 18 cm⁻¹ for a monolayer MoS₂ and confirms that the sample is a few-layer MoS₂ as desired for electrocatalytic study conducted below. As for other samples, with increasing MoS₂ content the difference in frequency of these modes increased marginally by 3–4 cm⁻¹ which is sufficient to warrant the increase in number of layers. Also provided is the intensity ratio of LA(M) mode at ~226 cm⁻¹ and E_{2g} mode at ~382 cm⁻¹ i.e., I_{LA(M)} to I_{E_{2g}} (see Fig. 5(B)), an indirect measure of defects in MoS₂ layers. Interestingly, the ratio is higher for MoS₂mono sample as compared with the hybrid aerogels, but the difference is marginal.

Significant structural changes occurring during the chemical and hydrothermal processing from pristine GO and rGO followed by MoS₂@GNS hybrid aerogels formation reflected in Raman spectra is also shown in Figure 5(A) (right panel). The Raman spectra of the pristine GO and rGO samples besides other hybrid samples display prominent G (E_{1g} symmetry) peak which is shifted to 1594 cm⁻¹ (ca. 1581 cm⁻¹ for graphite) and D (A_{1g} symmetry) band at ~1350 cm⁻¹. The G band originates from in-plane vibration of sp² C atoms and it is a doubly degenerate (TO and LO) phonon mode at the BZ (Brillouin Zone) center and D band is a Raman-forbidden and usually activated by defects related single-phonon inter-valley and intra-valley scattering process. Other bands are second-order D band (2D) occurs due to double resonance Raman process involving inter-valley scattering of an electron, basically related to the electronic band structure, a combination D + G band and second-order G (2G) band at approximately 2680 cm⁻¹, 2920 cm⁻¹ and 3180 cm⁻¹, respectively. Qualitatively, while relatively narrow G band

Figure 4. (A) UV-Visible absorption and zoomed region of spectra showing graphene and MoS₂ relevant peaks (B) a series of photoluminescence excitation (PLE) spectra and corresponding PLE maps of as-synthesized MoS₂, CrGO, 40, 60, 80 and 90 wt.% MoS₂ aerogels along with multilayer MoS₂ from monolayers dispersed in DI water. The PLE data was acquired at each of the labeled excitation wavelengths (λ_{ex}) with 30 nm interval until 450 nm.

indicates structural or crystalline order, the presence of a finite D band originates from the large density of defects (such as edges, grain boundaries, vacancies, implanted or substituted hetero atoms, and changes associated with carbon hybridization, sp^3 C) in all of the graphene-MoS₂ aerogels characterized. For a realistic comparison, the spectra are normalized to G band. Figure 5(B) summarizes the structural evolution in the Raman spectra for all the samples prior to and post mesoporous graphene-MoS₂ aerogels formation [41]. Extensive efforts have been made to study the relationship between the amount and nature of defects and intensity (and area) ratios of D, G and 2D

bands besides position variation in prominent Raman signatures. The D band position (ω_D) decreases with addition of MoS₂ from 1338 cm^{-1} to 1328 cm^{-1} for the aerogels studied in this work. On the other hand, G band position (ω_G) increases from 1592 cm^{-1} to 1600 cm^{-1} with MoS₂ addition. The 2D peak (ω_{2D}) downshifts from 2674 for GO and rGO_{th} to $\sim$ 2660 cm^{-1} for hybrid aerogels indicative of charge transfer at the heterointerfaces referred as *n*-type doping similar to nitrogenated graphene-based aerogels [41]. The second-order G band (ω_{2G}) position also changes in response to structural complexity and modification towards an upward trend (3150–3178 cm^{-1}).

Figure 5. (A) Micro-Raman spectra of graphene-MoS₂ aerogels showing graphene (D, G, 2D, D+G, 2G) and MoS₂ (A_{1g} and E_{2g} peaks) related Raman signatures; (B) variation of Raman spectral bands in terms of difference in MoS₂ A_{1g} and E_{2g} peak position along with SSEM micrograph, D, G, 2D and 2G band position (ω_D, ω_G, ω_{2D}, ω_{2G}), intensity ratio of D to G band (I_D/I_G) and 2D to G band (I_{2D}/I_G) (C) Raman spectral intensity ratio (I_D/I_G) maps for CrGO, 40, 60, 80 and 90 wt.% MoS₂ aerogel samples.

The marginal decrease in full-width at half maximum D band and G band for graphene-based aerogels is indicative of higher crystallinity of nanosheets resulting in the decrease of phonon lifetime (τ_{ph}) albeit qualitative. It is well documented that the intensity ratio of D to G band (I_D/I_G) is a semi-quantitative measure of structural order. Under the assumption the defect density is sufficiently lower (i.e., below critical concentration), the D band scattering intensity is proportional to the number density of point defects and the average inter defect distance. We noted that for all the hybrid aerogels, the I_D/I_G decreases with increasing MoS₂ content as compared with GO and rGO_{th} precursors and reaching the level of CrGO aerogel. This change suggests an increase in the average size of sp^2 bonded carbon (sp^2C) domains/cluster upon reduction following TK relation [41] and transformation to graphene aerogels. Alternatively, the introduction of MoS₂ content increased defects in carbon lattice with the highest I_D/I_G (1.6) that is slightly decreased with increasing MoS₂. It can also be explained as if new sp^2C domains are created albeit smaller in size and more in number density to those present in precursor graphene oxide. Also shown in Figure 5(B) is the plot of intensity ratio of 2D to G band for all the aerogels and increasing trend with MoS₂ content indicates higher ordering of graphene nanosheets. The observed shifts and the increase of the 2D peak intensity indicate that the graphene-based aerogels are of higher quality noting that the GO and rGO are successfully transformed into aerogels in the presence of MoS₂ nanosheets forming hybrids. Spatial maps of the Raman intensity (I_D/I_G) clearly show distribution of graphene nanosheets in combination with MoS₂ nanosheets (see Fig. 5(C)). However, due to local variations in film thickness and stacking disorder, mapping frequencies of MoS₂ modes do not allow direct determination of the number of layers. This also exemplifies the evolution of structural parameters in layered materials in changing from 2-dimensional to 3-dimensional crystalline mesoporous regime.

3.3. Electrochemical Hydrogen Evolution and Advanced Electrochemical Properties Determining Electron Transfer Rates of Graphene-MoS₂ ‘Hybrid’ Aerogels

Following morphological and structural characterization, we now focus on the electrochemical and electrocatalytic hydrogen evolution properties of as-synthesized aerogels with and without electrochemical desulfurization. It has been established that in most of the two-dimensional layers, basal plane (defect-free) are inactive toward any catalytic reactions [71]. However, it is found that formation of heterostructures, where dissimilar atomic layers are placed in contact with one another using multiple ways, can drastically change the inherent electrocatalytic activities of individual layers toward certain reactions, even leading to the activity of a basal plane that otherwise was inactive.

Moreover, with several advantages of emergent graphene nanomaterials such as tunable morphology and tailorable structure shown in Ref. [41], graphene-MoS₂ multifunctional hybrid aerogels studied here are applicable as novel electroanalytical platforms. Also, it is demonstrated theoretically that active sites could be directly created on basal plane of 2H-MoS₂ nanosheets by generating sulfur (S)-vacancies, whose intrinsic activity can be optimized by fine tuning the S-vacancy concentration and elastic tensile strain. To this end, prior to investigating hydrogen evolution, we created sulfur atom vacancies electrochemically (EC). Basically, it involves reducing the sulfur atoms in the basal plane of a few-layer 2H-MoS₂ as well as aerogels to form hydrogen sulfide (H₂S) gas via a desulfurization ‘activation’ cycle, similar to the oxygen vacancies generated in metal oxides under applied cathodic potential [72]. We also measured room temperature dc electrical conductivity (σ_{dc}) of the samples studied in this work shown in Figure 6(A). Almost all the samples showed semiconducting behavior with reasonable average σ_{dc} values ranged 0.1–8 S cm⁻¹ with spatial electrical heterogeneity since they were measured at various points on the samples. Figure 6(B) shows the variation of current density (chronoamperometry curves in interval of 1 min) with EC desulfurization duration of 10 min at various potentials for representative few layer MoS_{2mono} and 80 wt.% MoS₂ aerogel samples deposited on graphite rod and gold substrates. It acts as a post-synthesis activation procedure. The magnitude of current density increases with increasing negative potential from –1.0 to –2.0 V versus RHE suggesting the formation of presumably S-related defects. Some of the samples were also measured at –0.5 V and –0.7 V, but there was only a marginal change in current density (not shown). The various defects species in MoS₂ samples are majority sulfur vacancy and minority disulfur vacancy, molybdenum vacancy, double disulfur vacancy, dislocation, substitutional Mo on two sulfur sites and substitutional Mo on a sulfur site [73]. Such point defects, in particular, have been found to modify the local atomic structure, tailor physical-chemical properties and allows tunable electrochemical activity (EA). The relative current density increment defined as $\Delta j/j_0$, where j_0 is the current density at –0.3 V versus RHE before desulfurization, is plotted in Figure 6(C) for all the samples studied. It is apparent that few-layer MoS_{2mono} and 60 wt.% MoS₂ samples showed a pronounced improvement of about 300% and 60%, respectively. Interestingly, post-desulfurization activity in terms of current density was the least for 100 wt.% MoS₂ aerogel which may be resulting due to some what structurally unstable MoS₂ aerogel unlike for those combined with graphene nanosheets and for continuous multilayer MoS₂ films.

Typical cathodic polarization curves (j – E) and corresponding Tafel slopes are shown in Figure 7. The current densities are normalized to the geometric area of

Figure 6. (A) Room temperature current versus voltage (*I*–*V*) plots (left) and corresponding variation in dc electrical conductivity (σ_{dc}) at several points on the sample along with average values for CrGO, 40, 60, 80, 90 wt.% MoS₂ and MoS₂ aerogels along with GO and rGO_{th} precursors (B) representative amperometric curves (current density *j*–time *t*) for electrochemical desulfurization of MoS₂ and 80 wt.% MoS₂ aerogels showing current density increment versus desulfurization at various desulfurization voltages –1.0 to –2.0 V versus NHE and (C) current density increment versus desulfurization voltage at fixed desulfurization duration of 10 min for all the samples. The current density increment is defined as $\Delta j/j_0$, where j_0 is the current density at –0.32 V versus RHE before desulfurization.

the exposed face of all samples. Tafel plots are used to determine two important parameters describing HER activity of catalysts following Tafel equation: $\eta = \text{blog}|j| + j_0$, where η is overpotential, *j* is the current density, *a*

is exchange current density, namely, Tafel slope (b) and exchange current density. The exchange current density j_0 , is determined by fitting the linear portion of Tafel plot at low cathodic current. The linear part of the Tafel plot

under small overpotential yields a Tafel slope of 59 mV/s, which is smaller than the 120 mV/s from MoS₂. Due to increased number of edge sites, the exchange current densities of edge-terminated films are about five times higher than previous MoS₂ nanoparticle-based electrodes and compare favorably to most common metal catalysts. The similar HER activity between MoS₂ and MoS₂ supported on graphene suggests the Mo atoms are likely the main active centers on the edges, as already observed in hydro desulfurization reaction. The Tafel slopes measured from multiple samples are in the range of 105–120 mV/decade with smallest Tafel slope ~77 mV/decade for 60 wt.% MoS₂, high current density, and good stability was achieved with desulfurization. The latter suggests that the rate-determining step is the Volmer reaction, a discharge step that converts protons into adsorbed hydrogen atoms on the catalyst surface (Fig. 7(C)). Previous studies are shown a larger spread of Tafel slopes ranging from 40 to 120 mV/decade. A smaller Tafel slope, which is a useful metric to assess the performance of the catalysts and at the same time is a valuable indicator of the mechanistic reaction processes of HER [74], is desired for practical application of HER catalysts. Though Tafel slope alone is insufficient to determine the specific mechanism of HER, the results (Fig. 7(B)) are corroborated with those recent reports. The long-term stability is assessed by taking continuous cyclic voltammograms in the cathodic potential window at an accelerated scanning rate of 50 mV/s. The obvious variation is due to the active site density and a higher active site density. One can see these catalysts show much larger exchange current density and a relatively lower Tafel slope without any additives. Because rate of reaction is directly proportional to the number of edge sites for all samples, regardless of MoS₂ flake size, we conclude that the edge site is indeed the active site demonstrated below.

The electrochemical behavior of MoS₂@GNS hybrids as active electrode materials are investigated by cyclic voltammetry (CV) and *ac* EIS measurements. Comparative studies were performed on multilayer MoS₂, graphene oxide and CrGO aerogel. Figure 8(A) shows the CV curves at different scan rates ranging from 10 to 100 mV/s of MoS₂ aerogel, 40, 60, 80 wt.% of multilayer MoS₂ samples in +0.5 to −1.2 V potential window showing qualitative pseudo capacitive behavior and reversible Faradaic reactions. As the scan rate increases, the current response increases accordingly and the peak position changes, but the shape of CV curves retains, which indicates a good electrochemical stability and rate performance of the MoS₂@GNS aerogel due to carbon skeleton. The specific capacitance determined follows the equation, $C_s = I/mv$, I is the peak current, m the mass of active electrode materials and v is scan rate that are plotted in Figure 8(B) with scan rate for as-synthesized and desulfurized samples showing high specific capacity of 300 F·g^{−1}

(or 320 F·g^{−1}) for 90 wt.% MoS₂ (desulfurized) aerogel followed by 80, 40 and 60 wt.% MoS₂ samples in decreasing order. This indicates the presence of high quality few-layer graphene sheets embedded within or decorated with MoS₂ (S-vacancies induced by desulfurization) without restacking and aggregation during processing and higher performance is attributed to surface and edge functional groups in graphene nanosheets including nanowall edge sites and sulfur vacancies induced by desulfurization in MoS₂ nanosheets and central Mo atoms with multivalent from +2 to +6 during redox cycling (and charging and discharging) processes. Interestingly, multilayer MoS₂ and 100 wt.% MoS₂ showed the lowest specific capacitance of 30 F·g^{−1}. The analysis of quasi-reversible or heterogeneous ion transport current behavior helped to determine D governed by Randles–Ševčík equation for a reversible transfer process (Fig. 8(C)), $I_{\text{rev}} = 0.446FAC(FDv/RT)^{0.5}$ or $I_{\text{rev}} = (2.69 \times 10^5)n^{3/2}ACD^{1/2}v^{1/2}$, where A is the geometric area of the electrode (cm²), F is the Faraday Constant (C·mol^{−1}), D is the diffusion coefficient (cm²·s^{−1}), C is the concentration (mol/cm³), v is the scan rate (V·s^{−1}), R and T are usual constants, and n is the total number of electrons transferred in the electrochemical process. There is significant increase in D values for desulfurized 40, 80 and 90 wt.% MoS₂ hybrid aerogels found as opposed to CrGO, 100 wt.% MoS₂ and multilayer MoS₂ electrodes. It is attributed to tunable surface morphology, defect density and pore distribution at meso/nanoscale thus permitting access to numerous hydrophilic edges as well as basal plane defects, shorter pathways for fast and efficient ion transportation. Electrochemical impedance spectroscopy (EIS) was employed to gain further insight into the interface reaction, electrode kinetics, faradaic resistance and capacitive traits of MoS₂@GNS hybrid towards HER. The representative Nyquist, Bode–Bode plots and phase plots are shown in Figure 8(D) and Nyquist plot has two regions; quasi-semicircular and linear region. At higher frequency, the equivalent series resistance (R_s), including the ionic resistance of the electrolyte and intrinsic resistance of the material, is represented by the intercept of quasi-semicircle with the X-axis while the charge transfer resistance (R_{ct}) results from the faradaic reaction and double-layer capacitance (C_{dl}) at electrode/electrolyte interface that is calculated from the diameter of semicircle. Therefore, from Nyquist plots, the R_s of 4–7 Ω for all the samples studied decreased with desulfurization. As the ionic resistance of the electrolyte is the same, the decreasing R_s is led by the smaller intrinsic resistance of the electrode material, which could be inferred that the introduction of graphene could enhance the dispersion of MoS₂ so as to reduce the resistance, and the composition with CrGO could reduce the material resistance. The R_{ct} obtained by fitting with equivalent Randles' circuit ranged between 2–4 Ω which is marginally decreased with desulfurization to 1–2 Ω. Such is due to the fact that

Figure 7. (A) Linear sweep voltammetry (LSV) of MoS₂, 40, 60, 80, 90 wt.% aerogels and multilayer MoS₂ on carbon rod before (solid) and after (dotted) electrochemical desulfurization. The current densities (*j*) are defined based on the total electrode surface area. (B) Overpotential (η) and Tafel slope determined from each curve in (A) are plotted as histogram along with some literature values for comparison.

hierarchical structures of the hybrid nanocomposite aerogels allow facile ion and electron transfer, which further leads to the high electrocatalytic performance for HER. At low frequency, the nearly linear and vertical straight line which is almost parallel to imaginary axis with the largest slope shows that graphene/MoS₂ aerogels has pure capacitive behavior with least internal resistance. This conclusion is in compliant with the capacitance properties above mentioned and transition observed through phase behavior (Fig. 8(D)).

Intrigued by our findings, we interrogated the electrode surface by SECM (Scanning Electrochemical Microscopy). Since edge plane sites are considered far more reactive than the basal plane sites shown recently [75], it became critical to increase the relative edge plane sites for increased electrolyte exposure via 'vertical' nanowalls and increased defects number density in basal plane (via inducing S-vacancies) for enhanced heterogeneous electron transfer (HET) rate pertaining to

HER. Here in this work, SECM was used to obtain local quantitative information of reaction rates, to probe ion transport dynamics, and to determine electro active adsorption sites density distribution prior to and post-desulfurization. By detecting redox reactions occurring in a small region in close proximity to electrode surface (probe approach and feedback modes) with redox probe (also known as titrand), SECM monitors electrochemical (ionic and electronic) currents to be mapped and chemical reactivity correlating with the morphological structure as opposed to other scanning probe microscopy. Moreover, identification of active sites in heterogeneous catalysis requires a combination of surface sensitive methods and reactivity studies. We determined the first-order heterogeneous electron transfer rates (k_{ET}) following probe approach technique for all the aerogel samples. The tip is polarized at sufficient potential (+0.4 V) to ensure electrochemical redox reaction (re-generated) and the current was recorded (collected) over

Figure 8. (A) Representative cyclic voltammograms (CV) for MoS₂, 40, 60, 80 wt.% aerogels and multilayer MoS₂ at scan rates 10, 20, 50, 100 mV/s in base electrolyte 0.5 M H₂SO₄ before and after desulfurization (B) variation of specific capacitance (C_s) versus scan rate and (C) diffusion coefficient (D) as histogram (D) (top) Nyquist (−Im vs. Re Z) (middle) Bode–Bode (magnitude Z) and (bottom) phase behavior with log frequency plots for as-synthesized CrGO, MoS₂, 40, 60, 80, 90 wt.% aerogels electrodes in 0.5 M H₂SO₄ electrolyte before and after desulfurization. The Randles' equivalent circuit is shown in inset.

the polarized electrode surfaces at two polarities (i.e., pol1 and pol2) to determine k_{ET} and visualize electrochemical activity in feedback mode. The potassium ferricyanide; K₃Fe(CN)₆ is a surface-sensitive redox probe that is able to distinguish among different nanoscale materials including

functionalized graphene surfaces, which is usually not possible with an outer-sphere (electron transfer reaction that involves no bond breaking or bond formation process during redox processes) ruthenium hexamine (Ru(NH₃)₆ redox probe [41, 75]. Figure 9 shows probe approach

curves with normalized tip current and working electrode–probe tip distance ($L = d/a$). A Pt ultramicroelectrode (radius, $a = 10.0\ \mu\text{m}$) with $\text{RG} = 2$ was adopted as the SECM tip. The tip electrode current (i_T) reaches asymptotic behavior with steady-state current following: $i_{T,\infty} = 4nFCDa$, where n is the number of electrons transferred at the electrode tip ($\text{O} + n\text{e}^- \rightarrow \text{R}$), F is Faraday's constant, C is the concentration or flux of oxidized species, and D is the diffusion coefficient limited by the hemispherical region in microelectrode configuration. The feedback tip ion current is dependent upon the HET capability of the local areas. When $L = d/a \leq 1$, the normalized feedback current increases gradually or rapidly with increasing defect density, edge sites and functional groups. With the tip approaching the conductive electrode surface, the reduced species formed at the tip is oxidized, resulting in increased tip current following: $i_T > i_{T,\infty}$, $i_T^{\text{cond}}(L) = i_T/i_{T,\infty} = [k_1 + k_2/L + k_3 \exp(k_4/L)]$ that creates a regenerative “positive” feedback loop. The opposite effect is observed when scanning an insulating (or semiconducting, such as in this study) surface and diffusion to the electrode is inhibited due to physical obstruction, creating a “negative” feedback loop and decreasing the tip current i.e., $i_T < i_{T,\infty}$, $i_T^{\text{ins}}(L) = i_T/i_{T,\infty} = 1/[k_1 + k_2/L + k_3 \exp(k_4/L)]$ [76]. Alternatively, the Helmholtz region can be evaluated by changing the electrode polarity (equivalent to depth profile in electron microscopy and confocal microscopy) and strength of the tip voltage with respect to substrate [77].

The probe approach or feedback curves were fitted and plotted as dashed curved in Figure 9(A) deducing heterogeneous kinetic rate constant at the tip, k_{ET} (or k_1 in equations above). Qualitatively, the MoS₂@GNS aerogel electrodes generated two times larger ion current signals than those electrochemically desulfurized samples suggestive of increased local defects density beyond critical concentration. Other noteworthy features are related to subtle differences in their probe approach profiles depending upon the electrode polarization and specifically for 80 wt.% MoS₂ sample in which the tip current decreases rapidly i.e., within short electrode–tip separation distance thereby implying thinner outer Helmholtz plane. Figure 9(B) shows k_{ET} ($\text{cm} \cdot \text{s}^{-1}$) variation as histogram for all of the samples studied peaking for 40 wt.% and 80 wt.% MoS₂ depending upon polarity and state of desulfurization. The k_{ET} values ranged 1.0×10^{-1} – $1.0\ \text{cm s}^{-1}$ are within an accuracy of $\sim 0.1\%$, which is smaller than the typical experimental uncertainty. These are higher than those of reported values for pristine chemical vapor deposited graphene monolayers (2.0×10^{-2} – 4.2×10^{-2}) in aqueous solution [78]. The difference is attributed to tunable morphology, structural quality, basal and edge site defects density in MoS₂ aerogels interlaced with graphene aerogel nanosheets. Figure 9(C) displays SECM images ($250\ \mu\text{m} \times 250\ \mu\text{m}$) displaying probe tip current distribution as two-dimensional contour ‘heat maps’ and

three-dimensional images with ion current peaking occasionally reflecting high electroactivesites distribution. The imaging allows electrochemical current to be mapped at high spatial resolution across a surface for correlation with the corresponding structure and properties of electrodes surface. It is clearly observed that the normalized feedback currents are different from sample to sample upon the surface morphology and defects number density and also that of pristine multilayer MoS₂. Conventional wisdom indicates that higher is the feedback current, the faster is the local HET rate. However, while correlating the k_{ET} with number defect density *albeit* qualitatively, there is no systematic trend since k_{ET} first increases and then decreases and again increases with increasing MoS₂. Nevertheless, it is apparent that the samples yielded regions of higher electroactivity with areal site density (~ 30 – $50\ \mu\text{m}^2$), reinforcing the multiple roles played by MoS₂ and graphene complex aerogels. These findings underscore the significance of multivalent transition metal disulfides and topological multiplex morphology as high-performance electrochemical and catalytical systems related to the edge plane and basal plane defects as electroactive sites. This experimental approach helps to determine an optimal electroactivity with an upper bound defect density. It also suggests a broad distribution of k_{ET} (and current magnitudes) from samples studied and there will be some cross contribution at some single point measurements (from probe approach) where the tip is at the boundary between nanosheets, the different connectivity within nanosheets could also play a role in the broadness of k_{ET} kinetics similar to graphene AB stacking order [79]. Due to the dissimilar layers, there is an in-built electric field formed besides stacking disorder, layer sequencing or which layer is exposed to the electrolyte or analyte, affects the net catalytic performance [80].

Here we expand our discussion on advanced electrochemical characterization and correlation with electrocatalytic HER. The material system is at the resting state at the beginning of SECM with the molybdenum in MoS₂ aerogel and multilayer films in their Mo⁴⁺ oxidation states and the ferricyanide solution is in its reduced form; therefore, no reaction occurs. The redox species of interest Mo–H and $[\text{MoS}_2\text{–H}]^{2-}$ are generated by a reducing potential to the substrate electrode and the reaction begins by generation of the probe Fe⁴⁺ ions at the tip electrode by oxidizing potential (see Fig. 9(B)). The reaction between Fe⁴⁺ and Mo–H delivers a feedback current until the full consumption of the redox probe specie is monitored at the tip electrode and integration over time should yield the surface density of Mo–H. The delay between these reaction occurrences allow protons in solution consume the Mo–H ($[\text{MoS}_2\text{–H}]^{2-}$) by HER leads to decreased feedback current (similar to probe approach curve profiles) with time and analyzing the integrated charge yields the HER rate constant of Mo–H with protons (see Fig. 7(C)).

Figure 9. Continued.

Figure 9. (A) Probe approach curves showing normalized tip electrode current with tip-substrate normalized distance for MoS₂, 40, 60, 80, 90 wt.% aerogels and multilayer MoS₂ electrodes indicating semiconducting behavior at solid/liquid interface in redox mediator 5 mM K₃Fe(CN)₆ in support electrolyte 0.1 M PBS under (left) polarity 1: tip voltage $V_t = +0.5$ V, substrate voltage $V_s = -0.4$ V and (right) polarity 2: $V_t = +0.5$ V, $V_s = +0.4$ V (B) tip generation of redox probe as titrant, consumption of titrands (Mo–H) by titrants and HER by Mo–H as intermediate specie in the absence of titrants (C) heterogeneous electron transfer rate constant (k_{ET}) before and after desulfurization determined from empirical fitting probe approach profiles (D) representative SECM images (250 $\mu\text{m} \times 250 \mu\text{m}$) area of CrGO, MoS₂, 40, 80 wt.% MoS₂ and multilayer MoS₂ samples displaying probe current distribution in three dimensions with occasional higher/lower current reflecting “highly reactive” electroactivity under same conditions as probe approach curves. A color bar is shown for quantitative values of the tip current.

It should be noted that the hydride (and carboxyl) formation on the surface is assumed based on a recent theoretical study [81]. The “intrinsic activity” (i.e., per-site turnover frequency, TOF) is the catalyst activity on a per-site basis related to fundamental equation [5, 33]: $j(\eta) = i(\eta)/A = [\sum_{x=1}^S TOF_x(\eta)] \cdot nF/AN_A = S \cdot \overline{TOF} \cdot nF/AN_A$, where j is catalytic current density, i catalytic current, A surface electrode area, S number of surface sites, n number of electrons transferred per molecule, 2 for HER, F faraday constant, 96,458 (C/mol electrons), N_A Avogadro’s number, 6.022×10^{23} (mol^{−1}), and $\overline{TOF}$ average turnover frequency of all sites (s^{−1}) and therefore contribute to the molecular level *structure-property-function* relationships necessary to guide catalyst development. Although the MoS₂ nanostructure catalysts provide high active density, there is plenty of room available to enhance further their electrocatalytic activity. Among the layered Van der Waal (VdW) solids, it is worth mentioning that there is a different principle that goes beyond the locally active site optimization that is by utilizing topological electronic states to spur catalytic activity. In a recent report, the researchers found excellent catalytic activity in transition metal mono-pnictides–NaP, TaP, NbAs and TaAs–topological Weyl semimetals [82]. This study

suggested that the combination of robust topologically protected surface states and large carrier mobility originating from bulk Dirac bands of the Weyl semimetal, is a recipe for high activity of HER catalysts. This approach has the potential to go beyond graphene based composite electrocatalysts and photocatalysts where graphene simply provides a high mobility medium without any active catalytic sites that has been found in these topological materials. This work also provided a guiding principle for the discovery of novel catalysts from the emerging field of topological materials [83].

3.4. Theoretical Considerations for Correlating HET Rates and HER of MoS₂-Graphene Aerogels

The k_{ET} between different mesoporous graphene and other related materials and K₃Fe(CN)₆ can be described by the Gerischer-Marcus model in Eqns. [84]: $k_{ET} = v_n \int \varepsilon_{red}(E) f(E) \text{DOS}_G(E) W_o(\lambda, E) dE$ and $W_o(\lambda, E) = 1/\sqrt{4\pi kT} \exp(-(E - (E^0 + \lambda))^2/(4\lambda kT))$, where v_n is the nuclear frequency factor, $\varepsilon_{red}(E)$ is the proportionality factor, $f(E)$ is the fermi function, DOS_G is the electronic density of states of graphene, $W_o(\lambda, E)$ is the probability density function of the oxidized (unoccupied) states and λ is the reorganization energy of K₃Fe(CN)₆ in solution.

Figure 10. DFT optimized geometries obtained using the PBE0 functional for (A) the hydrated MoS₂ unit cell (2H configuration) at various water coverages (in ML). (a) Pristine, (b) 1 S vacancy, (c) 2 S 'hole'-type vacancies, (d) 2 S non-adjacent vacancies, and (e) 2 S adjacent vacancies MoS₂. Black and red values refer to charge transferred per unit cell from the water molecules towards the support using Mulliken and iterative Hirshfeld populations, respectively. Dashed and solid circles show surface vacancy and hole locations, respectively. The thin black lines denote unit cell boundaries. Atoms are colors as follows: S, yellow; Mo, green; O, red; H, white. (B) MoS₂/graphene unit cells. The S and C vacancies approximate locations are denoted by red and blue dotted circles, respectively. Double arrows show the distances from the S plane to the C plane. Values inside parenthesis refer to HSE06 calculations. C atoms are gray.

The electron transfer kinetics is determined by the integration of the number of electronic states of graphene and the number of oxidized states of K₃Fe(CN)₆ near the Fermi level for a reduction reaction [85, 86]. Alternatively, the improved k_{ET} can be understood by the presence of finite electronic DOS in the vicinity of Fermi level (E_F) and promoted reaction kinetics at the edges and interfaces. Figure 10 shows optimized geometries for various nanostructures described below.

3.5. Hydrated MoS₂

Our calculated MoS₂ structural parameters are within the range of the experimentally recorded value and past computational reports for dry MoS₂ (PBE0 calculations, Table I). We found that both PBE0 and HSE06 calculations produce similar geometries that is calculated MoS₂ structural parameters vary no more than 0.005 Å between these calculations. The presence of S vacancies in the MoS₂ affect its structural parameters and may lead to deformations. The defective MoS₂ lattice parameters and the Mo–S distance close to an S vacancy appears contracted relative to their values in the pristine MoS₂ case. For example, the presence of a single S vacancy on the MoS₂ support shortens the lattice parameter by about 0.03 Å and the Mo–S distance in the S vacancy region by about 0.08 Å. Hydration minimally affects pristine MoS₂ structural parameters, whereas it elongates the defective MoS₂ lattice parameters (Table I). Water dissociation appears in the case of its adsorption on defective MoS₂ (Figs. 10A(c–e)). At 0.375 ML water coverage, iterative Hirshfeld calculations on hydrated pristine MoS₂ show charge transfer from the waters towards the support, whereas Mulliken population shows the opposite. Recall that Mulliken population calculations are more sensitive to the basis set selection than the iterative Hirshfeld calculations. Therefore, the iterative Hirshfeld method will be the standard for studying charge

transfers here, whereas Mulliken populations are reported for comparison purposes. In the defect MoS₂ cases, both the iterative Hirshfeld and Mulliken calculations show that charge is transferred from the defective support toward the water molecules. These include the cases that H₂O has dissociated into OH and H (Fig. 10(A)) which in-turn increases HER. Large charge transfers of $>1.5e$ from the MoS₂ support towards the water molecules and their constituents appear in the case of hydrated defective MoS₂ with two S non-adjacent surface vacancies (Fig. 10A(d)).

3.6. Hydrated Pristine MoS₂/Graphene Heterostructure

The dry pristine MoS₂@graphene heterostructure has been studied previously, both computationally and experimentally. Kadantsev and Hawrylak [87] found that the distance between MoS₂ and graphene is about 3.4 ± 0.1 Å using scanning high-resolution transmission electron microscopy (STEM). Moreover, using micro-Raman spectroscopy and angle-resolved photoemission spectroscopy (ARPES), they detect no significant charge transfer between MoS₂ and graphene, which may not prevail under all conditions. Computationally, the MoS₂-graphene distance for the dry pristine MoS₂/graphene was reported in the range of 3.11–4.32 Å [88]. Here, our MoS₂-graphene distance is 3.13 Å and 3.14 Å, for the HSE06 and PBE0 calculations, respectively. Singh et al. [84] attributed the disagreement between calculated and experimentally observed MoS₂-graphene distances to the insufficient description of the weak van der Waals MoS₂-graphene interactions by the semi-empirical methods. It is observed that for the dry and hydrated MoS₂/graphene heterostructures, the presence of S vacancies on the top MoS₂ layer shorten the MoS₂-graphene distance (Fig. 10(B)). Both the PBE0 and HSE06 calculations show similar MoS₂/graphene optimized geometries. The calculated dry pristine MoS₂/graphene heterostructure C–C and Mo–S distances are 1.397 Å and 2.344 Å, respectively (PBE0 calculations). The former distance is shorter than the 1.411 Å value for the isolated graphene (mismatch $< 1\%$), whereas the latter is longer than the 2.330 Å value for the isolated MoS₂ (mismatch $\sim 0.6\%$). It is observed that waters are adsorbed on the pristine heterostructure without being dissociated (Fig. 10(B)).

3.7. Hydrated Defective MoS₂/Graphene Heterostructure

The presence of vacancies in the graphene monolayer cause out-of-plane deformations, as expected [89, 90]. Figure 10(B) shows that one of the 3 waters are dissociated, when adsorbed on defective MoS₂ surfaces. However, no water dissociation is observed, when waters adsorbed on pristine MoS₂ overlaid on defective graphene (Fig. 10B(d)). Water adsorption and dissociation on MoS₂ edges was studied by Ghuman et al. [91] who found that

Table I. The α and β in-plane lattice parameters and the smaller of the Mo–S distances for DFT optimized MoS₂ under various configurations, calculated with the PBE0 functional.

MoS ₂ configuration	Water coverage (ML)	α	β	Mo–S
Å				
Pristine	none	3.07	3.07	2.33
		(3.16 ²⁷ , exp.;		2.4219 ³⁰ ,
		3.119–3.24 ^{27–29} ,		2.415 ³¹ ,
		calc.)		calc.
	0.375	3.07	3.07	2.33
1 S vacancy	none	3.04	3.04	2.26
	0.4	3.05	3.05	2.27
2 S vacancy	none	3.02	3.02	2.31
(single “hole” formation)	0.4	3.04	3.07	2.29
2 S adjacent vacancies	none	3.01	3.04	2.24
	0.429	3.05	3.05	2.22
2 S non-adjacent vacancies	none	3.03	3.04	2.26
	0.273	3.06	3.07	2.28

water will dissociate spontaneously at room temperature on the Mo-edge site in addition to finite DOS (not shown). We must state that we are not aware of past computational studies on defective MoS₂/graphene heterostructures and these unprecedented results provide guidance towards the role of S-vacancy in improving HER.

4. CONCLUSIONS

In summary, three-dimensional network of graphene aerogel supported MoS₂ nanosheets have been successfully synthesized using facile hydrothermal–solvothermal technique for hydrogen evolution reaction. More importantly, the current synthesis route is much easier and cheaper without using any noble metals. The ensemble with varying MoS₂ content displayed well-organized architectures with layered MoS₂ nanosheets uniformly distributed around the pores of graphene aerogel or graphene nanosheets. They also featured good electrical conductivity by means of decreased contact resistance. The unique three-dimensional meso-/nanoporous architecture and large active surface areas facilitated faster ion diffusion (mass transport) and lead to superior HER activity with relatively lower overpotential and high catalytic exchange current density for electrochemically desulfurized samples. Moreover, MoS₂@GNS also exhibited good stability in acid solution, indicating the importance of the stable framework provided by 3D graphene aerogel framework. In addition, it showed the origin of the activity that is closely related to the amount of edges in the layered MoS₂. As a result of higher surface area with more exposed edge sites (higher edge plane surface area/total surface area), an excellent catalytic HER activity is demonstrated. The adjacent S vacancy defects-induced increase in density of states, dissociation and confinement of water molecules at the edge and planar S-vacancy sites calculated using density functional theory helped in establishing improved heterogeneous electrocatalytic rate, supported with combined measurements. Overall, we demonstrate conclusively that this study allowed to design graphene-MoS₂ heterostructure interfaces, understand their interaction through optical absorption and Raman spectroscopy (RS), to correlate among structure (via RS and optical spectroscopy), heterogeneous electron transfer rate (via scanning electrochemical microscopy; SECM) and hydrogen evolution reaction (via electrochemistry) quantitatively. These results were compared with continuous multilayer MoS₂ films highlighting the multiple role of tunable structure, tailorable surface morphology and electronic properties.

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References and Notes

1. Fujishima, A. and Honda, K., **1972**. Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 238(5358), pp.37–58.
2. Stamenkovic, V.R., Mun, B.S., Arenz, M., Mayrhofer, K.J.J., Lucas, C.A., Wang, G., Ross, P.N. and Markovic, N.M., **2007**. Trends in electrocatalysis on extended and nanoscale Pt-bimetallic alloy surfaces. *Nature Materials*, 6, pp.241–247.
3. Lu, T.N.V. and Barbir, F., **1992**. Hydrogen: The wonder fuel. *International Journal of Hydrogen Energy*, 17, pp.391–400.
4. Veziroğlu, T.N. and Şahin, S., **2008**. 21st Century's energy: Hydrogen energy system. *Energy Conversion and Management*, 49, pp.1820–1831.
5. Kibsgaard, J., Chen, Z., Reinecke, B.N. and Jaramillo, T.F., **2012**. Engineering the surface structure of MoS₂ to preferentially expose active edge sites for electrocatalysis. *Nature Materials*, 11, pp.963–969.
6. Vilekar, S.A., Fishtik, I. and Datta, R., **2010**. Kinetics of the hydrogen electrode reaction. *Journal of the Electrochemical Society*, 157, pp.B1040–B1050.
7. Parsons, R., **1958**. The rate of electrolytic hydrogen evolution and the heat of adsorption of hydrogen. *Transactions of the Faraday Society*, 54, pp.1053–1063.
8. Zou, X. and Zhang, Y., **2015**. Noble metal-free hydrogen evolution catalysts for water splitting. *Chemical Society Reviews*, 44, pp.5148–5180.
9. Pletcher, D., **1984**. Electrocatalysis: Present and future. *Journal of Applied Electrochemistry*, 14, pp.403–415.
10. Elias, L., Cao, P. and Hegde, A.C., **2016**. Magneto-electrodeposition of Ni–W alloy coatings for enhanced hydrogen evolution reaction. *Royal Society of Chemistry Advances*, 6, pp.111358–111362.
11. Elias, L. and Hegde, A.C., **2016**. Modification of Ni–P alloy coatings for better hydrogen production by electrochemical dissolution and TiO₂ nanoparticles. *Royal Society of Chemistry Advances*, 6(70), pp.66204–66208.
12. James, B.D., Baum, G.N., Perez, J. and Baum, K.N., **2009**. *Technoeconomic Analysis of Photoelectrochemical (PEC) Hydrogen Production*. Report No. GS-10F-009J, published on U.S. DOE EERE, website: www1.eere.doe.gov/hydrogen_and_fuel-cells/pdfs/pec_technoeconomic_analysis.pdf (US Department of Energy, 2009).
13. Nielsen, J.R.R., Sehested, J. and Norskov, J.K., **2002**. in *Advances in Catalysis*, edited by B. C. Gates, H. Knozinger, Vol. 47, pp.65–139.
14. Sheng, W.C., Gasteiger, H.A. and Horn, Y.S., **2010**. Hydrogen oxidation and evolution reaction kinetics on platinum: Acid versus alkaline electrolytes. *Journal of the Electrochemical Society*, 157, pp.B1529–B1536.
15. Fujishima, A. and Honda, K., **1972**. Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 238(5358), pp.37–58.
16. Walter, M.G., Warren, E.L., McKone, J.R., Boettcher, S.W., Mi, Q.X., Santori, E.A. and Lewis, N.S., **2010**. Solar water splitting cells. *Chemical Reviews*, 110, pp.6446–6473.
17. Faber, M.S. and Jin, S., **2014**. Earth-abundant inorganic electrocatalysts and their nanostructures for energy conversion applications. *Energy & Environmental Science*, 7, pp.3519–3542.
18. Yan, H., Tian, C., Wang, L., Wu, A., Meng, M., Zhao, L. and Fu, H., **2015**. Phosphorus-modified tungsten nitride/reduced graphene oxide as a high-performance, non-noble-metal electrocatalyst for the hydrogen evolution reaction. *Angewandte Chemie International Edition*, 54, pp.6325–6329.

19. Wu, H.B., Xia, B.Y., Yu, L., Yu, X.-Y. and Lou, X.W., **2015**. Porous molybdenum carbide nano-octahedrons synthesized via confined carburization in metal-organic frameworks for efficient hydrogen production. *Nature Communications*, 6, Article No. 6512, DOI: 10.1038/ncomms7512.
20. Gupta, S., Carrizosa, S.B.B., McDonald, B., Jasinski, J. and Dimakis, N., **2017**. Graphene-family nanomaterials assembled with cobalt oxides and cobalt nanoparticles as hybrid supercapacitive electrodes and enzymeless glucose detection platforms. *Journal of Materials Research*, 32, pp.301–322.
21. DuBois, M.R. and DuBois, D.L., **2009**. The roles of the first and second coordination spheres in the design of molecular catalysts for H₂ production and oxidation. *Chemical Society Reviews*, 38, pp.62–72.
22. Armstrong, F.A., Belsey, N.A., Cracknell, J.A., Goldet, G., Parkin, A., Reisner, E., Vincent, K.A. and Wait, A.F., **2009**. Dynamic electrochemical investigations of hydrogen oxidation and production by enzymes and implications for future technology. *Chemical Society Reviews*, 38, pp.36–51.
23. Singh, A.K. and Xu, Q., **2013**. Synergistic catalysis over bimetallic alloy nanoparticles. *ChemCatChem Catalysis*, 5, pp.652–676.
24. Shiraishi, Y., Sakamoto, H., Sugano, Y., Ichikawa, S. and Hirai, T., **2013**. Pt–Cu bimetallic alloy nanoparticles supported on anatase TiO₂: Highly active catalysts for aerobic oxidation driven by visible light. *ACS Nano*, 7, pp.9287–9297.
25. Wang, M., Wang, Z.X., Gong, X. and Guo, Z., **2014**. The intensification technologies to water electrolysis for hydrogen production—A review. *Renewable & Sustainable Energy Reviews*, 29, pp.573–588.
26. Turner, J.A., **1999**. A realizable renewable energy future. *Science*, 285, pp.687–689.
27. Hinnemann, B., Moses, P.G., Bonde, J., Jørgensen, K.P., Nielsen, J.H., Hørch, S., Chorkendorff, I. and Nørskov, J.K., **2005**. Biomimetic hydrogen evolution: MoS₂ nanoparticles as catalyst for hydrogen evolution. *Journal of the American Chemical Society*, 127, pp.5308–5309.
28. Novoselov, K.S., Jiang, D., Schedin, F., Booth, T.J., Khotkevich, V.V., Morozov, S.V. and Geim, A.K., **2005**. Two-dimensional atomic crystals. *Proceedings of the National Academy of Sciences of the United States of America*, 102, pp.10451–10453.
29. Eda, G., Yamaguchi, H., Voiry, D., Fujita, T., Chen, M. and Chhowalla, M., **2011**. Photoluminescence from chemically exfoliated MoS₂. *Nano Letters*, 11, pp.5111–5116.
30. Geim, A.K. and Grigorieva, I.V., **2014**. Van der Waals heterostructures. *Nature*, 499, pp.419–425.
31. Ding, Q., Song, B., Xu, P. and Jin, S., **2016**. Efficient electrocatalytic and photoelectrochemical hydrogen generation using MoS₂ and related compounds. *Chem-Cell Press*, 1(5), pp.699–726.
32. Cummins, D.R., Martinez, U., Sherehiy, A., Kappera, R., Garcia, A.M., Schulze, R.K., Jasinski, J., Zhang, J., Gupta, R.K., Lou, J., Chhowalla, M., Sumanasekera, G., Mohite, A.D., Sunkara, M.K. and Gupta, G., **2016**. Efficient hydrogen evolution in transition metal dichalcogenides via a simple one-step hydrazine reaction. *Nature Communications*, 7, pp.11857–11867, DOI: 10.1038/ncomms11857.
33. Benck, J.D., Hellstern, T.R., Kibsgaard, J., Chakthranont, P. and Jaramillo, T.F., **2014**. Catalyzing the hydrogen evolution reaction (HER) with molybdenum sulfide nanomaterials. *ACS Catalysis*, 4, pp.3957–3971.
34. Lauritsen, J.V., Kibsgaard, J., Helveg, S., Topsøe, H., Clausen, B.S., Lægsgaard, E. and Besenbacher, F., **2007**. Size-dependent structure of MoS₂ nanocrystals. *Nature Nanotechnology*, 2, pp.53–58.
35. Kong, D.S., Cha, J.J., Wang, H.T., Lee, H.R. and Cui, Y., **2013**. First-row transition metal dichalcogenide catalysts for hydrogen evolution reaction. *Energy & Environmental Science*, 6, pp.3553–3558.
36. Yang, J. and Shin, H.S., **2014**. Recent advances in layered transition metal dichalcogenides for hydrogen evolution reaction. *Journal of Materials Chemistry A*, 2, pp.5979–5985.
37. Voiry, D., Yamaguchi, H., Li, J.W., Silva, R., Alves, D.C.B., Fujita, T., Chen, M.W., Asefa, T., Shenoy, V.B., Eda, G. and Chhowalla, M., **2013**. Enhanced catalytic activity in strained chemically exfoliated WS₂ nanosheets for hydrogen evolution. *Nature Materials*, 12, pp.850–855.
38. Wu, Z., Fang, B., Wang, Z., Wang, C., Liu, Z., Liu, F., Wang, W., Alfantazi, A., Wang, D. and Wilkinson, D.P., **2013**. MoS₂ nanosheets: A designed structure with high active site density for the hydrogen evolution reaction. *ACS Catalysis*, 3, pp.2101–2107.
39. Laursen, A.B., Kegnas, S., Dahl, S. and Chorkendorff, I., **2012**. Molybdenum sulfides—efficient and viable materials for electro- and photo-electrocatalytic hydrogen evolution. *Energy & Environmental Science*, 5, pp.5577–5591.
40. Gorgolis, G. and Galiotis, C., **2017**. Graphene aerogels: A review. *2D Materials*, 4, p.032001.
41. Gupta, S., Meek, R., Evans, B. and Henson, A., **2019**. Interplay of topologically interconnected mesoporous network and defects number density in improving electroactivity of graphene-single-walled carbon nanotube aerogels. *Journal of Applied Physics*, 125, p.174301.
42. Gyurcsányi, R.E., Jággerszki, G., Kiss, G. and Tóth, K., **2004**. Chemical imaging of biological systems with the scanning electrochemical microscope. *Bioelectrochemistry*, 63, pp.207–215.
43. Shao, X., Wang, K., Pang, R. and Shi, X., **2015**. Lithium intercalation in graphene/MoS₂ composites: First-principles insights. *The Journal of Physical Chemistry C*, 119, pp.25860–25867.
44. Dovesi, R., Saunders, V.R., Roetti, C., Zicovich-Wilson, C.M., Pascale, F., Civalieri, B., Doll, K., Harrison, N.M., Bush, I.J., D'Arco, P., Llunell, M., Causà, M., Noël, Y., Maschio, L., Orlando, R., Erba, A., Rérat, M. and Casassa, S., **2017**. *Crystal17 User's Manual*. Torino, Univ. Torino.
45. Shi, H., Eglitis, R. and Borstel, G., **2006**. *Ab initio* calculations of the BaF₂ bulk and surface F centres. *Journal of Physics: Condensed Matter*, 18, pp.8367–8381.
46. Gupta, S. and Dimakis, N., **2019**. Computational predictions of electronic properties of graphene with defects, adsorbed transition metal-oxides and water using density functional theory. *Applied Surface Science*, 467–468, pp.760–772.
47. Dimakis, N., Flor, F.A., Salgado, A., Adjibi, K., Vargas, S. and Saenz, J., **2017**. Density functional theory calculations on transition metal atoms adsorbed on graphene monolayers. *Applied Surface Science*, 421, pp.252–259.
48. Ernzerhof, M. and Scuseria, G.E., **1999**. Assessment of the Perdew–Burke–Ernzerhof exchange–correlation functional. *Journal of Chemical Physics*, 110, pp.5029–5036.
49. Adamo, C. and Barone, V., **1999**. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *Journal of Chemical Physics*, 110, pp.6158–6170.
50. Krukau, A.V., Vydrov, O.A., Izmaylov, A.F. and Scuseria, G.E., **2006**. Influence of the exchange screening parameter on the performance of screened hybrid functionals. *Journal of Chemical Physics*, 125, pp.224106–5.
51. Grimme, S., Antony, J., Ehrlich, S. and Krieg, H., **2010**. A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu. *Journal of Chemical Physics*, 132, pp.154104–18.
52. Peintinger, M.F., Oliveira, D.V. and Bredow, T., **2013**. Consistent Gaussian basis sets of triple-zeta valence with polarization quality for solid-state calculations. *Journal of Computational Chemistry*, 34, pp.451–459.
53. Mahmoud, A., Erba, A., El-Kelany, K.E., Rérat, M. and Orlando, R., **2014**. Low-temperature phase of BaTiO₃: Piezoelectric, dielectric, elastic, and photoelastic properties from *ab initio* simulations. *Physical Review B*, 89, pp.045103–9.
54. Laun, J., Oliveira, D.V. and Bredow, T., **2018**. Consistent Gaussian basis sets of double- and triple-zeta valence with polarization quality of the fifth period for solid-state calculations. *Journal of Computational Chemistry*, 39, pp.1285–1290.
55. Monkhorst, H.J. and Pack, J.D., **1976**. Special points for Brillouin-zone integrations. *Physical Review B*, 13, pp.5188–5192.

56. Gilat, G., **1972**. Analysis of methods for calculating spectral properties in solids. *Journal of Computational Physics*, *10*, pp.432–465.
57. Anderson, D.G., **1965**. Iterative procedures for nonlinear integral equations. *JACM*, *12*(4), pp.547–560.
58. Bultinck, P., Van Alsenoy, C., Ayers, P.W. and Carbó-Dorca, R., **2007**. Critical analysis and extension of the hirshfeld atoms in molecules. *Journal of Chemical Physics*, *126*, pp.144111–9.
59. Bader, R.F.W., **1998**. *Atoms in Molecules in Encyclopedia of Computational Chemistry*. UK, John Wiley and Sons, Vol. 1, pp.64–86.
60. Koritsanszky, T.S. and Coppens, P., **2001**. Chemical applications of X-ray charge-density analysis. *Chemical Reviews*, *101*, pp.1583–1628.
61. Mulliken, R.S., **1955**. Electronic population analysis on LCAO–MO molecular wave functions I. *Journal of Chemical Physics*, *23*, pp.1833–1840.
62. Davidson, E.R. and Chakravorty, S., **1992**. A test of the hirshfeld definition of atomic charges and moments. *Theoretica Chimica Acta*, *83*, pp.319–330.
63. Mak, K.F., Lee, C., Hone, J., Shan, J. and Heinz, T.F., **2010**. Atomically thin MoS₂: A new direct-gap semiconductor. *Physical Review Letters*, *105*, p.136805.
64. Chikan, V. and Kelley, D.F., **2002**. Size-dependent spectroscopy of MoS₂ nanoclusters. *Journal of Physical Chemistry Society*, *135*, pp.5998–6001.
65. Štengl, V. and Henych, J., **2013**. Strongly luminescent monolayered MoS₂ prepared by effective ultrasound exfoliation. *Nanoscale*, *5*, pp.3387–3394.
66. Gupta, S., Smith, T. and Banaszak, A., **2017**. Graphene quantum dots electrochemistry and sensitive electrocatalytic glucose sensor development. *Nanomaterials*, *7*, pp.301–320.
67. Verble, J.L. and Weiting, T.J., **1970**. Lattice mode degeneracy in MoS₂ and other layer compounds. *Physical Review Letters*, *25*, pp.362–365.
68. Wilson, J.A. and Yoffe, A.D., **1969**. The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties. *Advances in Physics*, *18*, pp.193–335.
69. Sánchez, A.M. and Wirtz, L., **2011**. Phonons in single-layer and few-layer MoS₂ and WS₂. *Physical Review B*, *84*, pp.155413–155416.
70. Lee, C., Yan, H., Brus, L.E., Heinz, T.F., Hone, J. and Ryu, S., **2010**. Anomalous lattice vibrations of single- and few-layer MoS₂. *ACS Nano*, *4*, pp.2695–2700.
71. Li, H., Yu, K., Li, C., Tang, Z., Guo, B., Lei, X., Fu, H. and Zhu, Z., **2016**. Charge-transfer induced highefficient hydrogen evolution of MoS₂/graphene cocatalyst. *Science Reports*, *5*, Article No. 18730.
72. Lee, H.Y., Cho, W.S., Oh, S.M., Wiemhofer, H.D. and Göpel, W., **2013**. Active reaction sites for oxygen reduction in La_{0.9}Sr_{0.1}MnO₃/YSZ electrodes. *Journal of the Electrochemical Society*, *142*, pp.2659–2664.
73. Hong, J., Hu, Z., Probert, M., Li, K., Lv, D., Yang, X., Gu, L., Mao, N., Feng, Q., Xie, L., Zhang, J., Wu, D., Zhang, Z., Jin, C., Ji, W., Zhang, X., Yuan, J. and Zhang, Z., **2015**. *Nature Communications*, *6*, Article No. 6293.
74. Thomas, J.G.N., **1961**. Kinetics of electrolytic hydrogen evolution and the adsorption of hydrogen by metals. *Transactions of the Faraday Society*, *57*, pp.1603–1611.
75. Gupta, S. and Carrizosa, S.B., **2016**. Insights into electrode/ electrolyte interfacial processes and the effect of nanostructured cobalt oxides loading on graphene-based hybrids by scanning electrochemical microscopy. *Applied Physics Letters*, *109*, pp.243903–1–5.
76. Bard, A.J. and Faulkner, L.R., *Electrochemical Methods, Fundamentals and Applications*, 2nd ed., New York, John Wiley and Sons.
77. Li, W., Tan, C., Lowe, M.A., Abruña, H.D. and Ralph, D.C., **2011**. Electrochemistry of individual monolayer graphene sheets. *ACS Nano*, *5*, pp.2264–2270.
78. Ritzert, N.L., Rodríguez-Lopez, J., Tan, C. and Abruña, H.D., **2013**. Kinetics of interfacial electron transfer at single-layer graphene electrodes in aqueous and nonaqueous solutions. *Langmuir*, *29*, pp.1683–1694.
79. Güell, A.G., Ebejer, N., Snowden, M.E., Macpherson, J.V. and Unwin, P.R., **2012**. Structural correlations in heterogeneous electron transfer at monolayer and multilayer graphene electrodes. *Journal of the American Chemical Society*, *134*, pp.7258–7261.
80. Biroju, R.K., Pal, S., Sharma, R., Giri, P.K. and Narayanan, T.N., **2017**. Stacking sequence dependent photo-electrocatalytic performance of CVD grown MoS₂/graphene van der Waals solids. *Nanotechnology*, *28*, p.085101.
81. Huang, Y., Nielsen, R.J., Chen, Z., Goddard III, W.A. and Soriaga, M.P., **2015**. The reaction mechanism with free energy barriers for electrochemical dihydrogen evolution on MoS₂. *Journal of the American Chemical Society*, *137*, pp.6692–6698.
82. Rajamathi, C.R., Gupta, U., Kumar, N., Yang, H., Sun, Y., Sub, V., Shekhar, C., Schmidt, M., Blumtritt, H., Werner, P., Yan, B., Parkin, S., Felser, C. and Rao Weyl C.N.R., **2017**. Semimetals as hydrogen evolution catalysts. *Advanced Materials*, *29*, p.1606202.
83. Sanju Gupta and Avadh Saxena, **2018**. in *The Role of Topology in Materials Science*, Springer Series in Solid-State Sciences. Vol. 189.
84. Singh, S., Espejo, C. and Romero, A.H., **2018**. First-principles investigation of graphene/MoS₂ bilayer heterostructures using Tkatchenko-Scheffler van der Waals method. *Physical Review B* *98*, DOI: 10.1103/PhysRevB.98.155309.
85. Heller, I., Kong, J., Williams, K.A., Dekker, C. and Lemay, S.G.J., **2006**. Electrochemistry at single-walled carbon nanotubes: The role of band structure and quantum capacitance. *Journal of the American Chemical Society*, *128*, pp.7353–7359.
86. McCreery, R.L. and McDermott, M.T., **2012**. Comment on electrochemical kinetics at ordered graphite electrodes. *Analytical Chemistry*, *84*, pp.2602–2605.
87. Kadantsev, E.S. and Hawrylak, P., **2012**. Electronic structure of a single MoS₂ monolayer. *Solid State Communications*, *152*, pp.909–913.
88. Rahman, I.A. and Purqon, A., **2017**. First principles study of molybdenum disulfide electronic structure. *Journal of Physics: Conference Series*, *877*, pp.012026–6.
89. Fitri, D.A. and Purqon, A., **2017**. Calculation study of electric properties on molybdenum disulfide by using density functional theory. *Journal of Physics: Conference Series*, *827*, pp.012071–5.
90. Wang, W., Yang, C., Bai, L., Li, M. and Li, W., **2018**. First-principles study on the structural and electronic properties of monolayer MoS₂ with S-vacancy under uniaxial tensile strain. *Nanomaterials*, *8*(2), pp.74–1–11.
91. Ghuman, K.K., Yadav, S. and Singh, C.V., **2015**. Adsorption and dissociation of H₂O on monolayered MoS₂ edges: Energetics and mechanism from ab initio simulations. *Journal of Physical Chemistry C*, *119*, pp.6518–6529.

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